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14. ABSTRACT

Two different approaches for modeling the clustering in rapidly expanding plumes have been reported in the literature. The first approach, known as the classical approach, takes its starting point from the classical nucleation theory (CNT) which is based on equilibrium thermodynamics.[1,2] The second one, known as the kinetic approach, treats nucleation as the process of kinetic chemical aggregation.[3] The first, macroscopic, approach, while being useful and found to be applicable for a number of flow scenarios, has at the same time a number of drawbacks that are very difficult to overcome. In many cases when CNT-based results cannot be fitted to experimental data. For example, the CNT-based prediction of the cluster size distributions[4] significantly deviated from experimental data.[5] This is also consistent with the work of Ref. 6, where it was also found that the correct prediction of the cluster size distribution along with the internal and translational energy distributions is beyond the area of applicability of the classical approach.

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Accuracy Analysis for Kinetic Modeling of Homogeneous Condensation in Plumes

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Two different approaches for modeling the clustering in rapidly expanding plumes have been reported in the literature. The first approach, known as the classical approach, takes its starting point from the classical nucleation theory (CNT) which is based on equilibrium thermodynamics.[1,2] The second one, known as the kinetic approach, treats nucleation as the process of kinetic chemical aggregation.[3] The first, macroscopic, approach, while being useful and found to be applicable for a number of flow scenarios, has at the same time a number of drawback that are very difficult to overcome. In many cases when CNT-based results cannot be fitted to experimental data. For example. the CNT-based prediction of the cluster size distributions[4] significantly deviated from experimental data.[5] This is also consistent with the work of Ref. 6, where it was also found that the correct prediction of the cluster size distribution along with the internal and translational energy distributions is beyond the area of applicability of the classical approach.

The reasons for the discrepancy between the CNT-based distributions and experimental data are both due to problems inherent in CNT and the flow conditions of expanding plumes. The former include the ambiguous definition of the surface energy of small clusters,[7] the negligence of the rotational and translational degrees of freedom of freshly nucleated clusters,[8] and the unrealistic description of vapor-cluster and cluster-cluster interactions.[16] The latter are related to the main assumptions underlying the derivation of the nucleation rate, which may be violated in rapidly expanding supersonic flows.[9] The transient time needed for a system to reach steady state in terms of the unimolecular cluster reactions may be such that the jet macroparameters will significantly change during that time. Moreover, many theoretical and experimental results[10–12] suggest that local thermal equilibrium does not exist in an expanding supersonic jet. Thus the process of cluster formation is not likely to be isothermal.

The second, kinetic, approach, is not limited by any assumption of thermodynamic equilibrium. This approach has generally a number of possible realizations, from mathematical models such as those based on the Smoluchowski equations, to computer modeling with the molecular dynamics method, to the use of methods of rarefied computational fluid dynamics, primarily the direct simulation Monte Carlo (DSMC) method. Of these techniques, only the latter is practical for numerical prediction of multi-dimensional flows of practical interest, such as thruster plume flows with homogeneous (and, generally, heterogeneous), condensation. The first two are prohibitively expensive computationally, even for modern parallel computers.

The DSMC method has been used to study the process of cluster formation and evolution for a number of years. In the earlier studies,[13–15] the gas flow in the was uniform, the considered cluster size range was very narrow (up to 25 monomers in a cluster) and the examined reaction types were unrealistically limited to elastic collisions, cluster and monomer sticking to clusters, and evaporation of monomers from clusters. More recently, the DSMC method has been extensively and successfully applied to modeling the processes of cluster formation and evolution in supersonic jets by Levin et al (see, for example, Refs. 16–18). The model initially was based on the classical nucleation theory, with the new clusters being formed at the critical size. Further work of these authors[19] extended the kinetic dimer formation approach of Ref. 20, who assumed

that a ternary collision always results in a dimer formation, to include molecular dynamic (MD) simulations for obtaining information on the probability of dimer formation in such ternary collisions. The work[21] used a temperature-dependent probability of formation of argon dimers.

Most recently, the first principle kinetic theory was used[22] to construct a DSMC based model that uses truly kinetic RRK model[23] is implemented to characterize the cluster evaporation rates, and an energy dependent collision procedure similar to the recombination reaction model of Ref. 24 for the collision complex formation. An empirical parameter was introduced for the inelastic collision number in the cluster-monomer collisions, and the Larsen-Borgnakke[25] principle was extended to simulate the energy transfer in collisions among monomers and clusters.

The recent studies have shown that while the application of the kinetical kinetic approach has a number of benefits, which include but linited to capturing non-equilibrium features of the condensation process and correct prediction of many condensation phenomena and rates (see, for example, Refs. 19, 22), they do suffer from large uncertainties in such key parameters that they use as heat capacities, binding energies, energy redistribution mechanism, and cluster inelastic collision number. Two important examples of the effect of these uncertainties are given below.

Consider first equilibrium rates of nucleation and equilibrium constants, that any condensation model should be able to capture reasonably well for the results to be reliable. Here, thermal bath relaxation of pure argon and pure water is examined using the kinetic model[22] at different temperature conditions, and the dimer recombination rates for argon and equilibrium constants for the formation of dimers in argon and water are calculated and compared to the published results.[26–28] The computed dimer formation rates and equilirbium constants are presented in Fig. 1, where they are compared with the corresponding theoretical predictions.

While the present recombination rates are in reasonable agreement with the classical trajectory calculations, the computed rates have visibly smaller slope than that of the theoritical analysis, both for argon and water. The factors affecting the slope are beleived to be the temperature dependence of the dimer stabilization probability and the heat capacity, that were not included in the model, as well as the evaporation energy value and the after-reaction energy redistribution (recall that the Larsen-Borgnakke model was used for the energy redistribution).
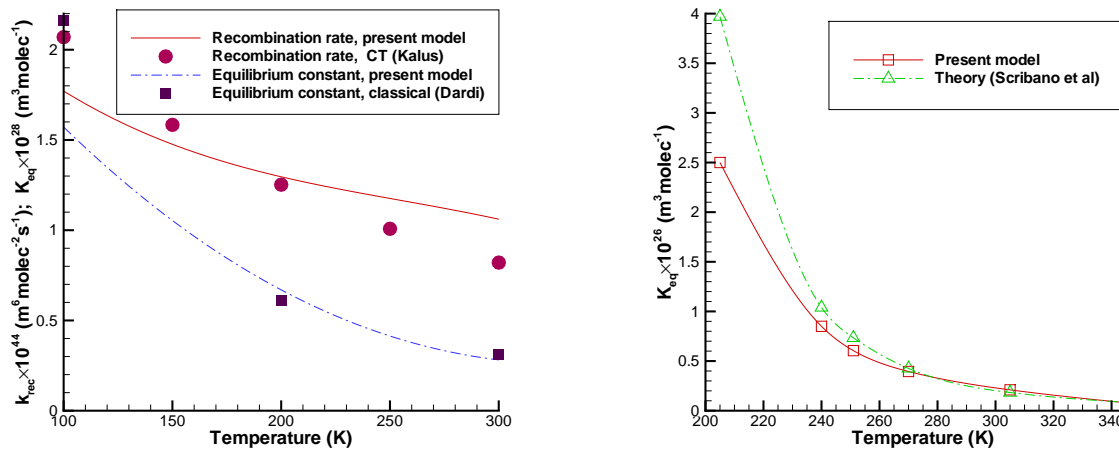

Figure 1. Argon dimer formation rate and equilibrium constant as functions of gas temperature (left), and water equilibrium constant as a function of gas temperature (right).

In addition to the above, an important factor that influences the magnitude of the equilibrium constant K_{eq} was found to be the probability of the energy transfer between the internal modes of a dimer and the translational modes in dimer-monomer collisions, Z^{-1}. This may be explained as follows. The dimers are formed after three-body collisions, and typically have internal energies smaller than the evaporation energy after those collisions. In argon, the evaporation energy for a dimer is relatively small compared to the typical

total collision energy for all temperatures under consideration ($E_{evap}/k \approx 70$ K). That means that most of the dimers will have their internal energy in excess of the evaporation energy just after one or two collisions with monomers. The lifetime of the dimers whose internal energy is larger than the evaporation energy is very short, on the order of a picosecond. This results in the dimer-monomer energy transfer being the main process that leads to quick dimer dissociation. Note that the value of Z has negligible impact on the dimer formation rates, and only the evaporation rates are affected. As a result, in the range of temperatures considered in this work, the equilibrium constant for argon was found to be nearly proportional to Z^{-1}. For example, at 200 K $K_{eq} = 0.11 \times 10^{-26}$ m^3/molec when $Z = 1$ is used, versus $K_{eq} = 0.66 \times 10^{-26}$ m^3/molec for the baseline case of $Z = 6$. For water molecules, Z dependence is smaller but still very significant.

The second example is a flow of condensing water molecules through a conical nozzle. The nozzle is a conical nozzle with a 41° opening angle, a total length of 2 mm, and a throat diameter of 50 μm.[29] A stagnation pressure of 1.577 bar and temperature of 495 is considered here. A sensitivity study has been conducted to estimate possible effect of parameters of the model. In addition to the baseline computation,[22] the cases with a larger $Z = 1$ (compared to the baseline of $Z = 6$) and smaller values of the cluster evaporation energies and cluster heat capacities (both decreased by 20%) were used. Note that these are relatively large changes that are believed to represent the limiting cases for the corresponding parameters. The cluster mole fractions for these four cases are presented in Fig. 2.

It is interesting to note that the mole fraction terminal value is only weakly sensitive to the varied parameters. It is about 1% for all cases under consideration. The transient behavior in the firs half of the nozzle significantly differs for these cases, though. The decrease in the heat capacity is in effect the decrease in the number of cluster internal degrees of freedom. Smaller number of internal degrees of freedom of a cluster means that when the Larsen-Borgnakke routine is used for energy redistribution (the energy is split proportionally to the number of degrees of freedom), it will take more collisions to raise the cluster's internal energy to the values exceeding the evaporation threshold. As a result, more clusters are present in the flow. When the cluster evaporation energy values are reduced, smaller number of clusters are observed in the flow, since they become easier to evaporate. The cluster internal energy relaxation number has relatively small effect on cluster populations.
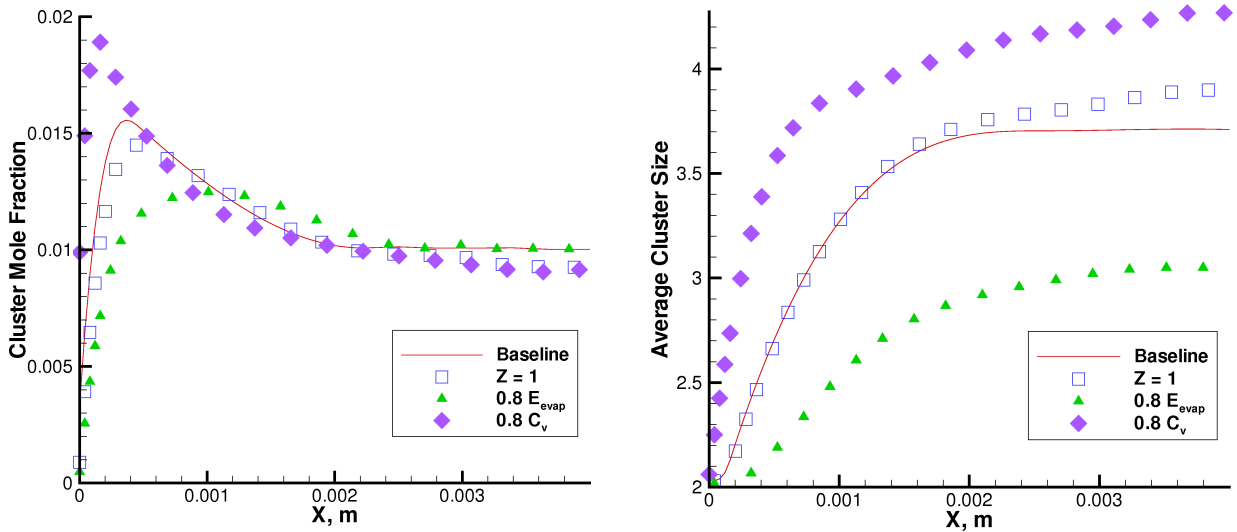

Figure 2. Cluster mole fraction, left, and average cluster size, right, along the nozzle axis for different parameters of the condensation model.

The above arguments for the impact of different parameters of the model are still applicable when the average cluster size is examined. Only the change in Z has relatively minor effect in this case. To the contrary, the decrease in the heat capacity significantly increases, and in evaporation energy, increases, the average cluster size. Note also that changing all three parameters seems to increase the relaxation length as compared to the baseline case, where the cluster fraction and size distribution come to their terminal values soon after the nozzle exit.

Comparison of the terminal size distribution obtained for the baseline model, with experimental results[29] is shown in Fig. 3. In the experiments, the dimers were below the detection threshold, the trimer population may be somewhat affected by that threshold, and all larger clusters are believed to be recorded without significant distortions. For side-by-side comparison, the experimental size distribution was normalized so that it has the same fraction of clusters larger than dimers as in the computation. The results show that while there is a reasonable agreement between the numerical modeling and measurements, there is a maximum for the cluster sizes of 5 and 6 observed in the computations, that were not recorded experimentally. The reason for this maximum is the corresponding maximum in the evaporation energies for these cluster sizes used in the present model. It appears that more accurate values of evaporation energies (only one water molecule orientation was considered in Ref. 30) have to be used to obtain better agreement with the data.
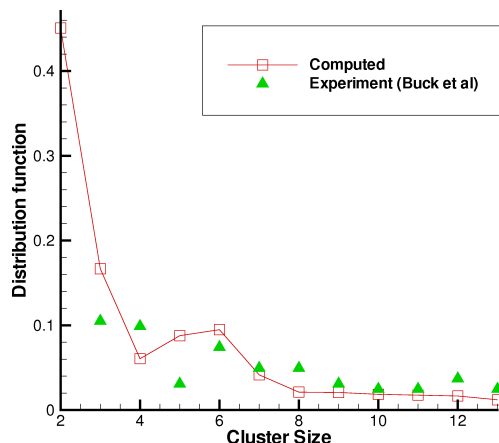

Figure 3. Comparison of the computed size distribution with experimental data of Ref. 29.

All this prompts the authors to carefully examine the accuracy of the model and its sensitivity to different parameters and to use the molecular dynamics approach in order to better understand the area of applicability and the accuracy of these parameters. Two pressure regimes are considered in this study. First is a relatively low pressure regime where the nucleation is driven by the cluster-monomer collisions, and the cluster size distribution is mostly two-temperature exponential. Second is a high pressure regime where the nucleation is driven by cluster-cluster collisions, and the cluster size distribution is log-normal. The validation of results will be conducted through comparison with measured water cluster size distribution in Ref.[29]

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